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The Relationship Between the TiO_2 Photocatalyst Deactivation, Regeneration and the Concentration of the Surface Adsorbed SO_4^{2-}

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Abstract. The photolysis ability and adsorption ability of TiO_2 was detected and measured using acetaldehyde as a probe. The quantitative relationship between the TiO_2 deactivation and the concentration of the surface adsorbed SO_4^{2-} was obtained by intentional controls of the concentrations of the surface adsorbed SO_4^{2-}. When the concentration of the surface adsorbed SO_4^{2-} reached 2.0 wt%, the photolysis ability of the TiO_2 photocatalyst decreased by 50%, and when the concentration was 2.9 wt%, the TiO_2 adsorption ability decreased by 50%. 90% of the absorbed SO_4^{2-} can be removed after the samples have been washed by overflowing water for 2 hours at a rate of 2 $L.min^{-1}$ and the photocatalytic activity can be regenerated. This work will help to predict the lifetime of TiO_2 photocatalyst in actual applications as well as to understand its regenerations of the photocatalytic capability.

Introduction

TiO_2 photocatalyst has been widely applied in the fields of air/water pollution degradations due to its cheapness, high activity and safety [1-5]. However, during the applications of such TiO_2 photocatalyst materials, the accumulations of some oxidization products onto the surfaces of TiO_2 will ultimately result in their deactivations [6]. The understandings of the TiO_2 deactivation and regeneration vs the adsorbed oxidization product compounds become very important in the prediction of the lifetime of the photocatalyst.

One of the most common oxidization products of various pollutions during many TiO_2 photo-degradation processes [7-10] is SO_4^{2-}, which would be adsorbed onto the surface of the TiO_2 photocatalyst, leading to its deactivations. Even though the adsorption of SO_4^{2-} onto the surfaces of the TiO_2 photocatalyst has been confirmed by FTIR [8] or XPS [9], and the mechanism of the deactivation of the TiO_2 photocatalyst by the SO_4^{2-} has also been studied [10], the quantitative relationship of the TiO_2 photocatalytic deactivation, regeneration and the concentration of the adsorbed SO_4^{2-} still remains a challenge.

The relationship of the TiO_2 photocatalytic deactivation, regeneration and the concentration of the adsorbed NO_3^- were investigated by using acetaldehyde as a probe in our previous work [11]. In this work, the quantitative relationship of the photocatalytic deactivation of the TiO_2 and the concentration adsorbed SO_4^{2-} and regenerations are studied by the same method.

Experimental

The TiO_2 photocatalyst (～10 nm particle diameter, 186 $m^2.g^{-1}$ BET area, anatase phase) was obtained by heating the commercial TiO_2 anatase powder (～6 nm particle diameter, 304 $m^2.g^{-1}$ BET area, Tayca Co.) under ambient atmosphere at 400 ℃ for 3 hours (h) to remove any possible adsorbed

substance from the TiO_2 surfaces before the further experiments. The heated TiO_2 powders were then immersed in a H_2SO_4 solution of 0.01, 0.1, or 1 $mol.L^{-1}$ for 1 h respectively, and dried at 120 ℃ for 1 h to prepare the TiO_2 photocatalyst samples with controlled concentrations of the adsorbed SO_4^{2-}.

The adsorption ability and photolysis ability of TiO_2 photocatalyst were then detected and measured using acetaldehyde as a probe. Acetaldehyde can be photo-decomposed by the TiO_2 photocatalyst to form CO_2 and H_2O according to the reaction formula (1) [12].

$$CH_3CHO + 5/2O_2 + h\nu \rightarrow 2CO_2 + 2H_2O \quad (1)$$

A gas-bag experimental was conducted and details of gas-bag method were in our previous work [11]. UV (365nm) irradiation strength was set to be 1.0 ± 0.1 $mW.cm^{-2}$ on those TiO_2 samples. The concentrations of CH_3CHO, CO_2 were detected by photo-acoustic multi gas monitor (Innova 1314) with a temperature at 25 ± 2℃.

The regeneration of the TiO_2 photocatalytic ability was carried on for a sample of 3 g at a water over-flowing rate of 2 $L.min^{-1}$. The concentration of the adsorbed SO_4^{2-} vs the washing time was obtained.

The concentrations of the adsorbed SO_4^{2-} were determined by the extraction method and the ion chromatograph described in details in reference 11.

Results and discussion

The concentrations of surface adsorbed SO_4^{2-} . There are about 5～130 $mg.L^{-1}$ adsorbed SO_4^{2-} on the surfaces of the commercial TiO_2 photocatalyst powders as received, and no adsorbed SO_4^{2-} within the detection limit after heated at 400 ℃ for 3 h. The sample after heated at 400 ℃ for 3 h was regarded as a sample with 0 wt% adsorbed SO_4^{2-}. The TiO_2 samples immersed in 0.01, 0.1, and 1 $mol.L^{-1}$ H_2SO_4 solutions have different concentrations of the adsorbed SO_4^{2-}, which are determined to be 1.0 wt%, 3.3 wt%, and 19.2 wt%, respectively, by the same extraction method. Note that there is not influence of the heating at 120℃ for 2 h on the absorption ability or photocatalytic capability of the treated samples.

Deactivation characteristics and the concentration of the adsorbed SO_4^{2-} . The result of the photocatalytic capability and the concentration of surface adsorbed SO_4^{2-} of the treated TiO_2 photocatalyst with different adsorbed SO_4^{2-} is shown in Figure 1, in which Figure 1(a) is the concentration change of the reactant acetaldehyde, and Figure 1(b) is the net production concentration of CO_2 after UV light irradiation (i.e. the total CO_2 concentration minus the presence of CO_2 before UV light irradiation). Note that "A" action point is when the CH_3CHO gas was injected into the testing-bag and "B" action point is when the UVA lamp was switched on.

The detected acetaldehyde concentrations between "A" and "B" (in dark room for 30 minutes) in Figure 1(a) indicate that: (1) The adsorption by the TiO_2 photocatalyst samples to the acetaldehyde decreases with the increases of the surface adsorbed SO_4^{2-}; and (2) The balance between adsorption and desorption of the acetaldehyde on the surfaces is reached at the end of 30 minutes in the dark room. The adsorption ability of the TiO_2 photocatalyst can be calculated by formula (2) [11]:

$$\eta_{Adsorb} = (C_{Before} - C_{After}) / C_{Before} \times 100\% \quad (2)$$

C_{Before} is the acetaldehyde concentration at "A" point; C_{After} is the acetaldehyde concentration after 30 minutes from "A" point (at "B" point).

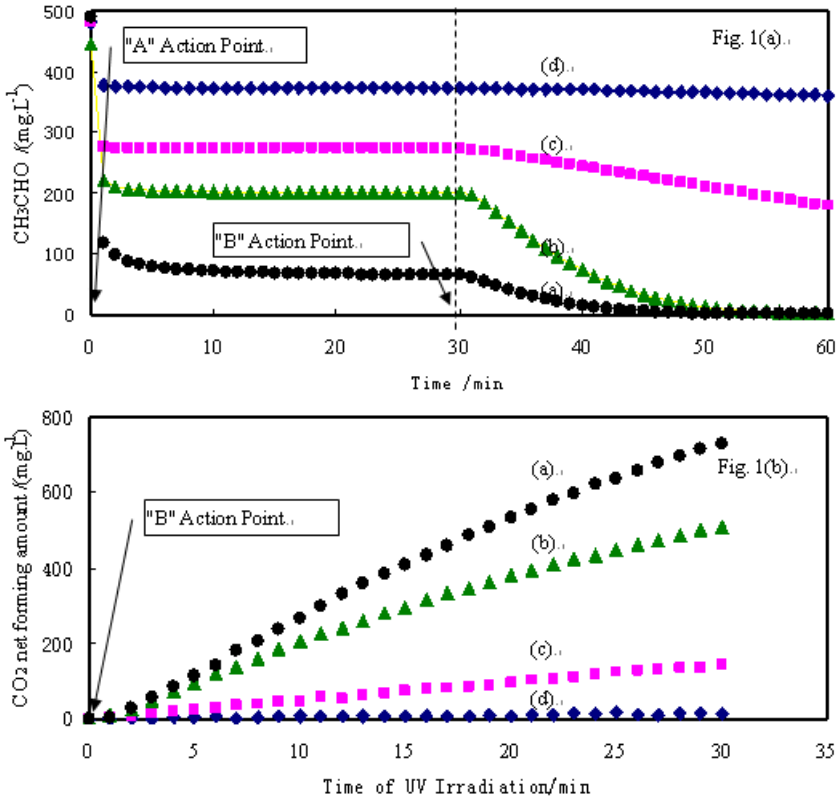

Fig. 1 Photocatalytic activity testing data of TiO_2 samples with the adsorbed SO_4^{2-} of (a) 0.0 wt%,(b) 1.0 wt%,(c) 3.3 wt% and (d) 19.2 wt%

After "B" point (when UV light was on) in Figure 1(a), lower concentrations of the adsorbed SO_4^{2-} samples of (a) and (b) result in an apparent decrease of the acetaldehyde and reach zero acetaldehyde concentration within 30 minutes after the UV irradiation, while higher concentrations of the adsorbed SO_4^{2-} samples of (c) and (d) have not apparent influence on the acetaldehyde concentrations. After 30 minutes of the UV irradiation, the reactant concentrations of acetaldehyde are still a lot greater than zero for the samples (c) and (d). It is clear that these samples (c) and (d) show photocatalytic deactivation. Especially for the sample (d), containing 19.2 wt% of the adsorbed SO_4^{2-}, the reactant concentration of the acetaldehyde has almost no changed after UV irradiation, indicating that the sample (d) has been completely deactivated.

The data of net production concentration of CO_2 in Figure 1(b) also indicate that the sample (d) with 19.2 wt% of the surface adsorbed SO_4^{2-} is complete photocatalytic deactivation since there is not much change in CO_2 production by UV irradiation. However, there are continuous increases in the CO_2 production by UV irradiation with both sample (a) of no adsorbed SO_4^{2-} and sample (b) of 1.0 wt% of the adsorbed SO_4^{2-} , of cause, sample (b) has a little lower CO_2 production than sample (a). The sample (c) of 3.3 wt% of the adsorbed SO_4^{2-} sits between these two ends. The CO_2 production by UV irradiation drops apparently showing its photocatalytic deactivation, but still has some degrees of the photocatalytic effect.

Within 30 minutes photo irradiation time, for both samples (a) and (b), although acetaldehyde concentrations reach zero, the CO_2 is still continuously produced. It indicates that the acetaldehyde or its middle substances have been adsorbed on the TiO_2 surface and have continued to be transformed to CO_2 by photo-oxidization. Under long time photo irradiation, the CO_2 production concentration eventually reached its saturated level (data not shown here). However, the concentration of the CO_2 net production have a very good linear relation to the photo irradiation time within the first 15 minutes after the UV light was on, seen in the Figure 1(b). Therefore, using the same data processing method

as reference [11], photolysis ability $\eta_{Photolysis}$ can be expressed by the mean CO_2 production rate within 15 min after "B" point, which means the acetaldehyde photocatalytic transforming rate to CO_2 with a unit of CO_2 $mg.L^{-1}.min^{-1}$.

Figure 2 is the plot of the adsorption ability η_{Adsorb} and photolysis ability $\eta_{Photolysis}$ vs the concentration of the adsorbed SO_4^{2-}, calculated from the data in the Figure 1. η_{Adsorb} and $\eta_{Photolysis}$ decrease sharply with the concentration of the adsorbed SO_4^{2-} from 0 to 3.3 wt%, and then keep decreasing further with more concentration of the adsorbed SO_4^{2-}. Experiments were repeated and the errors were estimated to be about 10%.

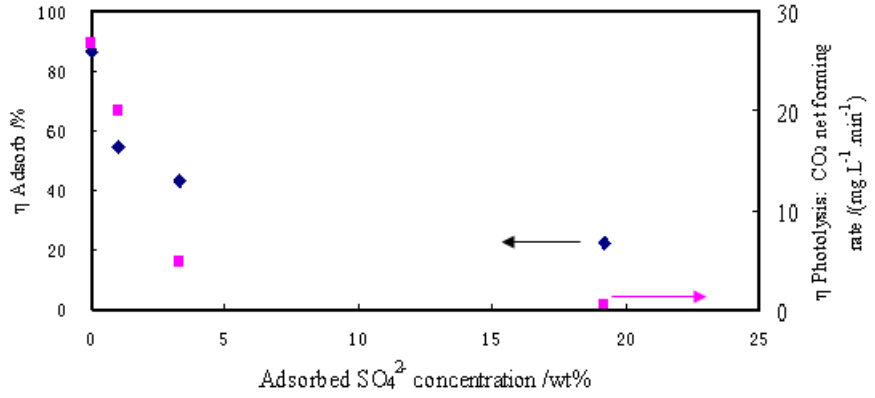

Fig. 2 The adsorption ability, photolysis ability vs the concentration of the surface adsorbed SO_4^{2-} on the TiO_2 samples

For the purpose to calculate the concentrations of the adsorbed SO_4^{2-} on the TiO_2 surface to responding to the TiO_2 adsorption ability and photolysis ability dropping by 50%, the drops of η_{Adsorb} and $\eta_{Photolysis}$ vs the concentration of the adsorbed SO_4^{2-}, using a standard of 100% as the sample (a) of no adsorbed SO_4^{2-}, is plotted in the Figure 3. The data between 0 to 3.3 wt% of the adsorbed SO_4^{2-} are used for the linear fittings, since the drops of η_{Adsorb} and $\eta_{Photolysis}$ were already over 50% for the sample (c) of 3.3 wt% of the adsorbed SO_4^{2-}. From the curve fitting formulas shown in Figure 3, TiO_2 adsorption ability and photolysis ability drop by 50% ($\eta_{Adsorb\ 50\%}$ and $\eta_{Photolysis\ 50\%}$) are corresponded to the concentrations of 2.9 wt% and 2.0 wt% of the adsorbed SO_4^{2-}, respectively.

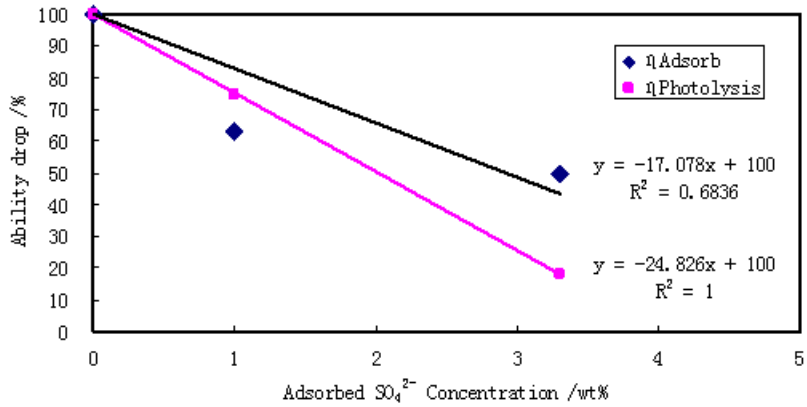

Fig. 3 The TiO_2 adsorption and photolysis ability vs the concentration of the surface adsorbed SO_4^{2-}

The fact that $\eta_{Adsorb\ 50\%}$ and $\eta_{Photolysis\ 50\%}$ correspond to different concentrations of the adsorbed SO_4^{2-} can be explained by their different mechanisms. Adsorption is a physical process, while photolysis is a chemical one (i.e. reaction formula 1). $\eta_{Photolysis\ 50\%}$ corresponds to a lower concentration of the adsorbed SO_4^{2-} than $\eta_{Adsorb\ 50\%}$. It indicates that the TiO_2 photolysis ability is a lot more easily influenced by the adsorbed SO_4^{2-} than the adsorption ability is. The conclusion is the same

as that of the TiO_2 photocatalytic deactivation vs the concentrations of the adsorbed NO_3^- [11]. The quantitative relationship of photocatalyst capability and the concentrations of the adsorbed compounds obtained for SO_4^{2-} here or for NO_3^- in previous work are essential to the prediction of the lifetime of TiO_2 photocatalyst in actual applications.

The chemical states of the adsorbed SO_4^{2-} on the surface of TiO_2 photocatalyst were also confirmed by Fourier transformation infrared spectroscopy (FTIR), shown in Figure 4. The samples were prepared by the KBr pallet method. For the sample (a) without adsorbed SO_4^{2-}, despite of a strong peak at 480 cm^{-1} for TiO_2, a broad absorption peak at 3440 cm^{-1} (attributed to O-H stretching vibration) and a peak at 1646 cm^{-1} (attributed to O-H bending vibration) are detected, the same as in reference 7. These O-H related peaks are possible due to the adsorbed water on the TiO_2 surface. For samples (b), (c) and (d), immersed into H_2SO_4 solution, a few of new peaks at 1151 cm^{-1} and 1053 cm^{-1} are detected, similar to the peaks at 1148 cm^{-1} and 1052 cm^{-1} in reference 7, corresponding to SO_4^{2-} and $S_2O_5^{-2}$ groups. In the meanwhile, for sample (d), there are peaks at 993 cm^{-1} and 1241 cm^{-1} (belonging to $S_2O_6^{-2}$ group). It is known that S-O and S=O bonds have FTIR absorption peaks between 900 cm^{-1} and 1500 cm^{-1} [7]. The relative strength of the peak at 1151 cm^{-1} is in the sequence of (d) > (c) > (b) as shown in Figure 4. Therefore, it is reasonably derived that SO_4^{2-} compounds are present in samples (b), (c) and (d), and that the SO_4^{2-} concentrations are in the order of (d) > (c) > (b). FTIR results are consistent with the detecting results of ion chromatograph.

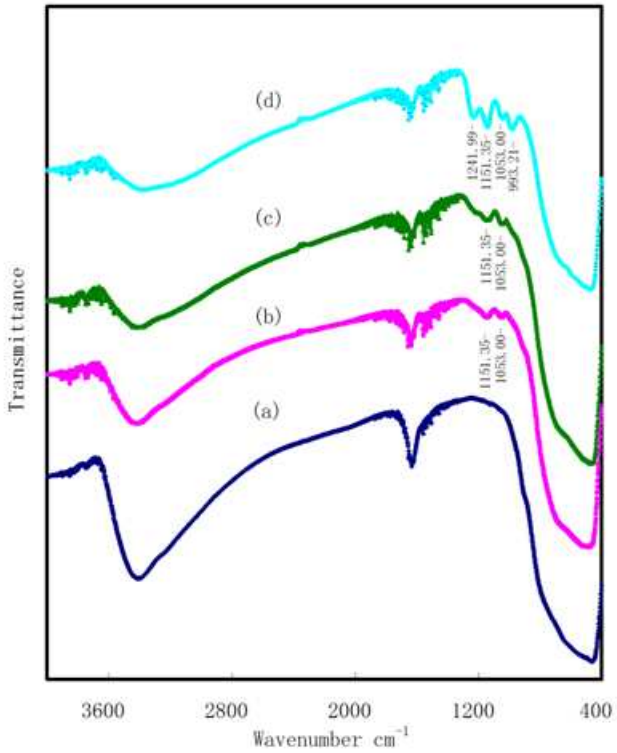

Fig. 4 FTIR spectra of (a) TiO_2 heated at 400 ℃ for 3 h; (b), (c) and (d): TiO_2 powder (a) immersed in 0.01, 0.1 and 1 $mol.L^{-1}$ H_2SO_4 for 1 h then dried at 120 ℃ for 1 h

Regeneration characteristics vs adsorbed SO_4^{2-}. Figure 5 shows the plot of residue concentration and removal percent of the adsorbed SO_4^{2-} vs water washing time under the water overflowing rate of 2 $L.min^{-1}$. The residue concentrations of the adsorbed SO_4^{2-} dropped sharply with the washing time, and the removal percent of adsorbed SO_4^{2-} reached 90% after water washing for 2 h. The adsorption ability and photolysis ability of the sample after water washing for 2 h are almost completely regenerated, respectively. It is confirmed that water overflow-washing is an effect method to remove the adsorbed SO_4^{2-} on the surfaces of the TiO_2 photocatalyst powders.

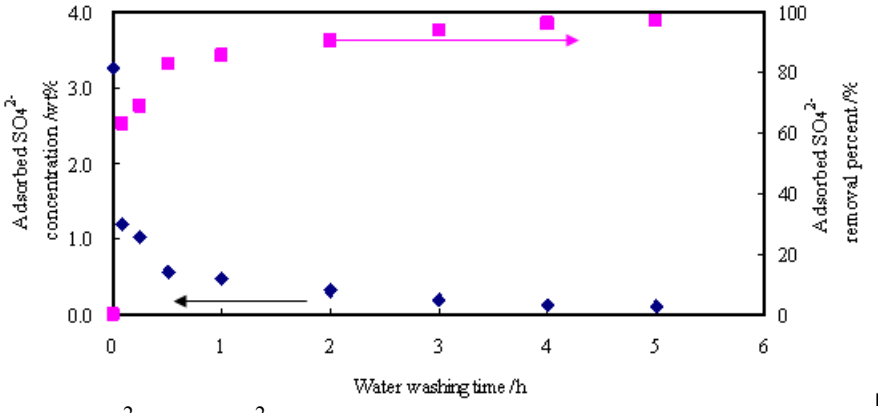

Fig. 5 The residual SO_4^{2-} and SO_4^{2-} removal percent vs water washing-time for the TiO_2 sample with adsorbed SO_4^{2-} 3.3 wt% under 2 $L.min^{-1}$ overflowing

Conclusions

TiO_2 photocatalytic deactivations of adsorption and photolysis abilities vs the concentration of the adsorbed SO_4^{2-} have been investigated by intentional controls of the surface adsorbed SO_4^{2-} on the TiO_2. Results show that the TiO_2 photolysis ability is more easily influenced by the adsorbed SO_4^{2-} than the TiO_2 adsorption ability. The photolysis ability drops by 50% when the concentration of the adsorbed SO_4^{2-} reaches 2.0 wt%, while the adsorption ability decreases by 50% when the concentration of the adsorbed SO_4^{2-} is about 2.9 wt%. Water overflow-washing is an effect method to remove the adsorbed SO_4^{2-} on the TiO_2 surface to regenerate the TiO_2 photocatalyst.

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